BIOPETROL SYHTHESIZED FROM STEARIC ACID – HETEROGENEOUS CATALYTIC CRACKING BY ZEOLITE

MOHAMAD NAQUIB FITRI BIN MOHD NADZRI

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**Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang**

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ABSTRACT

Biopetrol is the alternative way to reduce the application of using petroleum where it is a new technology that more environmental friendly and furthermore it is the latest finding in research after biodiesel, bio-ethanol and bio-butanol. Biofuel is defined as fuel produced from derivation of vegetable oils and specifically, biopetrol is defined as fuel which has the same characteristic with the petrol, but is produced from stearic acid that is contained in palm oil where the conversion of stearic acid is done to get the molecular formula and structure of isooctane. Due to reduction of fossil fuel, environmental issues, and rising of petrol price, biopetrol can be the alternative fuel to the fossil fuel. In this research, stearic acid are used as a raw material, catalytic cracking are method that used together with zeolite as a catalyst. The experiment starts with heating the Stearic Acid until it melts at 69.6^{o}C, and then 10 grams of zeolite being added and the heating process proceed until the temperature reached 98^{o}C as the isooctane produced at level 1.The next experiment is repeated with different level of speed at level 2, 3 and 4. All the product samples are analyzed with Gas Chromatographer (GC). The isooctane concentrations are increased when the speed of stirring are increased, but not obviously. From the result obtained from the Gas Chromatogram result, the percentage of actual concentration of isooctane obtained for level 1 is 5.873%, level 2 is 5.921%, level 3 is 5.886% and level 4 is 5.873%. These yields are much higher than the yields produced from normal catalytic cracking method which is from 3% to 6 %. It showed that the heterogeneous catalytic cracking method will produce much higher yields for biopetrol synthesized compared to normal catalytic cracking method. This experiment should be conducted in more proper dynamic method to optimize the yields.

ABSTRAK

Biopetrol adalah salah satu langkah alternatif bagi mengurangkan penggunaan minyak petroleum dari pelbagai aspek dan ia juga merupakan teknologi yang mesra alam selepas menemuan bio-diesel, bio-ethanol dan bio-butanol. Biofuel didefinisikan sebagai bahan api yang dihasilkan daripada terbitan oleh minyak sayuran. Secara spesifiknya biopetrol didefinisikan sebagai bahan api yang mempunyai sifat yang sama dengan petrol tetapi ia dihasilkan daripada asid palmitik di mana komposisinya banyak terdapat pada minyak sawit. Oleh kerana sumber bahan api fosil yang semakin kurang, isu alam sekitar, kenaikan harga petrol, biopetrol boleh menjadi bahan api alternatif kepada bahan api fosil. Dalam kajian ini, asid oleic digunakan sebagai bahan mentah, teknik penguraian dengan pemangkin digunakan serta ketulan kuprum sebagai pemangkin. Experimen di mulakan dengan memanaskan Asid Stearik sehingga menjadi cecair pada suhu 69.6^{o}C dan seterusnya ditambah dengan zeolite dan penasan diteruskan sehingga suhu mencecah 98^{o}C di mana isooktana yang sudah terbentuk sambil dikacau pada kelajuan pertama. Experimen diulang dengan menggunakan kelajuan putaran pada tahap 2, 3 dan 4. Semua sampel produk dianalisis dengan menggunakan *Gas Chromatographer*. Kepekatan isooktana yang dikehendaki akan bertambah apabila kelajuan putaran bertambah, tetapi tidak terlalu jelas. Daripada keputusan Gas Chromatogram yang diperolehi, peratusan kepekatan isooctana untuk kelajuan pertama adalah 5.873%, kelajuan kedua adalah 5.921%, ketiga 5.886% dan kelajuan keempat adalah 5.872%. Penghasilan ini adalah lebih tinggi daripada hasil yang diperolehi daripada penghuraian haba berkatalis biasa iaitu dari 3% kepada 6%. Ini menunjukkan kaedah penghuraian berkatalis dinamik adalah lebih baik. Eksperimen ini patut dijalankan dalam keadaan dinamik dengan cara yang lebih baik bagi mendapatkan hasil yang lebih optimum.

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CHAPTER I

INTRODUCTION

1.1 Introduction

Biofuel is referred as liquid or gaseous fuels that are produced recent dead biological mass and the fossil fuel also derived from long term dead biological material or predominantly called as biomass. Biopetrol is one kind of biofuel defined as fuel which has the same characteristics with commercial petrol in terms of its molecular formula.

Biofuel is suitable for vehicle fuel and had already been tested. Biofuel produced from natural vegetable oil or fats can be used as transportation fuel or fuel additive in the vehicles to reduce their emissions. Plant oils are attracting increased attention in this respect (Bhatia *et al*., 2003).

Biopetrol is one of biofuel and suitable for petrol vehicle consumer. During the future century, demand of petrol will rises due to increasing of vehicle consumer. Thus, something new need to be done to make sure fuel problem will not rise.

1.2 Identification of Problem

1.2.1 Petrol Oil Prices

Nowadays, the fuel price in Malaysia still high and keep increasing from day to day, but actually the global oil price is cheaper than the price in our country. This situation happens because of the crisis of world economy today. Refer to figure 1, although the crude oil price now decreasing but the trend kept increase from year to year.

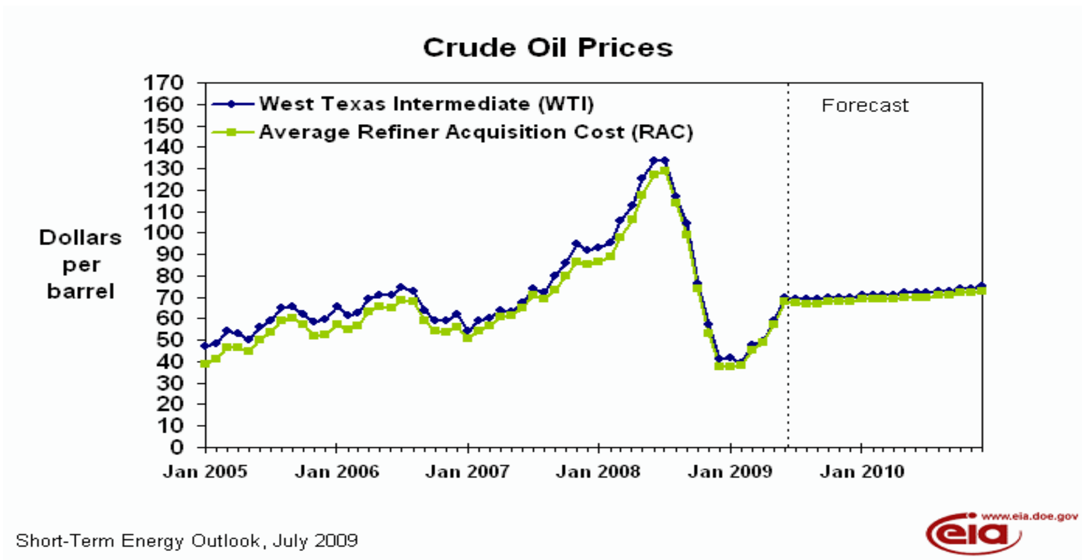


Figure 1.1: Price of World Crude Oil from January 1995 until now.

1.2.2 Air Pollution and Health

Driving a car is the most polluting act an average citizen commits. Combustion engines contribute to greenhouse gas accumulation in the atmosphere and are responsible for climate changes. Thus, long term solutions require that vehicles use less polluting energy sources such biofuels. Biofuels burned in diesel engines have a better environmental profile. Negative environmental consequences of fossil fuels and concerns about petroleum supplies have spurred the search for renewable transportation biofuels (Hill et al).

1.3 Objectives

Objective can be defined as guidance to make sure that the problem is solve with an appropriate solution. The objectives for this proposal are:

i) To improve the concentration of isooctane produced from stearic acid by using modified catalytic cracking method.

ii) To compare the yields of isooctane produced using the modified catalytic cracking method.

1.4 Scopes of Study

To make sure the objectives succeed, this research is focusing on the criteria that are stated as below:-

i) To describe the molecular arrangements of the substances in cracking

ii) To understand the catalytic cracking and distillation process.

iii) To apply the dynamism of catalytic cracking process.

iv) To determine the yield of desired isooctane component in the product through Gas Chromatography analysis.

1.5 Rationale and Significance

There are many advantages of biofuel which are:

i) Create a new development technology in biopetrol where it can apply for petrol-used vehicle engines.
ii) Biopetrol is an environmentally friendly alternative liquid fuel for current petrol.
iii) The CO_2 reduction potential of biofuels is enormous in comparison with fossil fuels.
iv) Biofuels are biodegradable

CHAPTER II

LITERATURE REVIEW

2.0 Definition of fuel

Fuel (from Old French *feuaile*, the combination phrase from *feu* (fire; ultimately from Latin focus fireplace, hearth) is a substance that may be burned in air (or any other oxidant-containing substance), i.e. that so quickly reacts with oxygen that heat and light is emitted in the form of a sustained flame. Usually 'fuel' and only refer to easily flammable substances in air (the air is the oxidiser needed by a fuel to burn, and it is needed in larger quantities than fuels, so, a first glance on it seems appropriate). . Fuels are used as convenient energy stores because of their high specific energy release when burnt with omnipresent ambient air.

By referring the World Encyclopedia (2008), the term fuel refers to substance that is burned or otherwise modified to produce energy, usually in the form of heat. Apart from fossil hydrocarbons (coal, oil and gas) and firewood and charcoal, the term also applies to radioactive materials used in nuclear power stations.

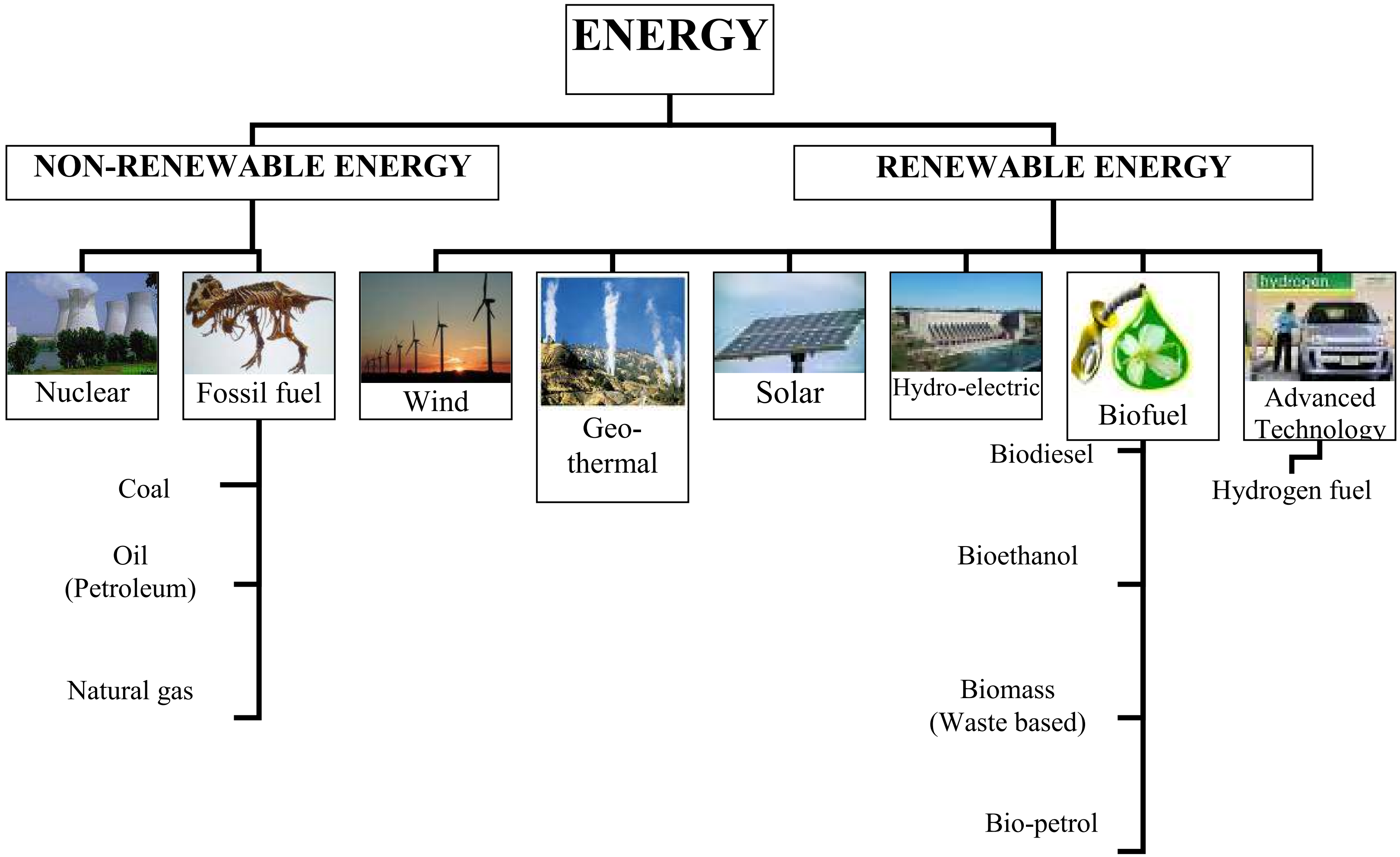


Figure 2.1 Energy's Classification

2.1 Biofuel

Biofuel is defined as liquid or gaseous fuel that can be produced from the utilization of biomass substrates and can be serving as a (partial) substitute for fossil fuels or can be broadly defined as solid, liquid, or gas fuel derived from recently dead material. As theoretically, biofuels can be produced form any biological carbon source. A variety of biofuels can be produced from biomass resources including liquid fuels, for example ethanol, methanol, biodiesel and biopetrol.

2.1.1 Types of Biofuel

2.1.1.1 Biodiesel

Biodiesel is a natural and renewable domestic fuel alternative for diesel engines made from vegetable oils, mostly soy and corn. It contains no petroleum, is nontoxic and biodegradable. It is made using an alcohol like methanol and a chemical process that separates glycerine and methyl esters (biodiesel) from fats or vegetable oils.

Biodiesel is made through a chemical process called transesterification whereby the glycerin is separated from the fat or vegetable oil. The process leaves behind two products -- methyl esters (the chemical name for biodiesel) and glycerin (a valuable byproduct usually sold to be used in soaps and other products).

2.1.1.2 Bioethanol

Bioethanol fuel is mainly produced by the sugar fermentation process, although it can also be manufactured by the chemical process of reacting ethylene with steam. Bioethanol which is also known as cellulosic ethanol or lignocellulosic or chee is not made from oils and fats but from lignocellulose, a structure material that consist mostly plant feedstock. Production of bioethanol used sources of sugar that come from fuel or energy crops.

Ethanol or ethyl alcohol is a clear colourless liquid, it is biodegradable, low in toxicity and cause little environmental pollution if split. Ethanol burns to produce carbon dioxide and water. It has high octane fuel and replaced lead as an octane enhancer in petrol. The most common blend is 10% ethanol and 90% petrol (E10). Blending ethanol with gasoline would oxygenated the fuel mixture and the result it would burns more completely and reducing pollution of emissions.

2.1.1.3 Biomass

The term "biomass" refers to any form of plant or animal tissue. In the energy industry, biomass refers to wood, straw, biological waste products such as manure, and other natural materials that contain stored energy. The energy stored in biomass can be released by burning the material directly, or by feeding it to micro-organisms that use it to make biogas, a form of natural gas. Energy from biomass is still used around the world, for everything from cooking and heating to generating electricity.

Using biomass can help reduce global warming compared to a fossil fuel-powered plant. Plants use and store carbon dioxide (CO2) when they grow. CO2 stored in the plant is released when the plant material is burned or decays. By replanting the crops, the new plants can use the CO2 produced by the burned plants. So using biomass and replanting helps close the carbon dioxide cycle. However, if the crops are not replanted, then biomass can emit carbon dioxide that will contribute toward global warming.

2.1.1.4 Biopetrol

Biopetrol is defined as fuel which has the same characteristics with commercial petrol in terms of its molecular formula. Petrol is a complex mixture of hydrocarbons which consists a mixture of C_4 to C_{10} alkanes. However isooctane ($C_{18}H_{18}$) as dominative component in petrol is assigned an octane number of 100. Isooctane or 2,2,4-trimethylpentane ($CH_3C\ (CH_3)_2CH_2CH(CH_3)CH_3$) burns smoothly with a little knock in petrol engine. It is the highest quality of petrol (Mansur, 2005:1).

Biopetrol from palm oil is biodegradable and non-toxic since from the environmental point of view, fuel from vegetable sources is environmentally friendly. It is able to suppress certain pollutants that come up from the exhaust, with the exception of NOx in certain cases, where unpredictable results occurred. From the technical point of view it can be said that biofuel (biopetrol) is technically compatible with the current internal combustion engine. Slight modification might be required to enhance the power. Biopetrol could be an answer to the future air emission control. The application of existing biodiesel from palm oil in motor vehicle has been proven to be successful (Prateepchaikul and Apichato, 2003).

2.2 Refining of Petroleum

Petroleum is a complex mixture of organic liquids called crude oil and natural gas, which occurs naturally in the ground and was formed millions of years ago. Crude oil varies from oilfield to oilfield in colour and composition, from a pale yellow low viscosity liquid to heavy black 'treacle' consistencies.

An oil refinery is an organised and coordinated arrangement of manufacturing processes designed to produce physical and chemical changes in crude oil to convert it into everyday products like petrol, diesel, lubricating oil, fuel oil and bitumen.

2.2.1 The refining process

The refinery begins with the separation of crude oil into different fractions by distillation. The fractions are further treated to convert them into mixtures of more useful saleable products by various methods such as cracking, reforming, alkylation, polymerisation and isomerisation. These mixtures of new compounds are then separated using methods such as fractionation and solvent extraction. Impurities are removed by various methods, e.g. dehydration, desalting, sulphur removal and hydrotreating.

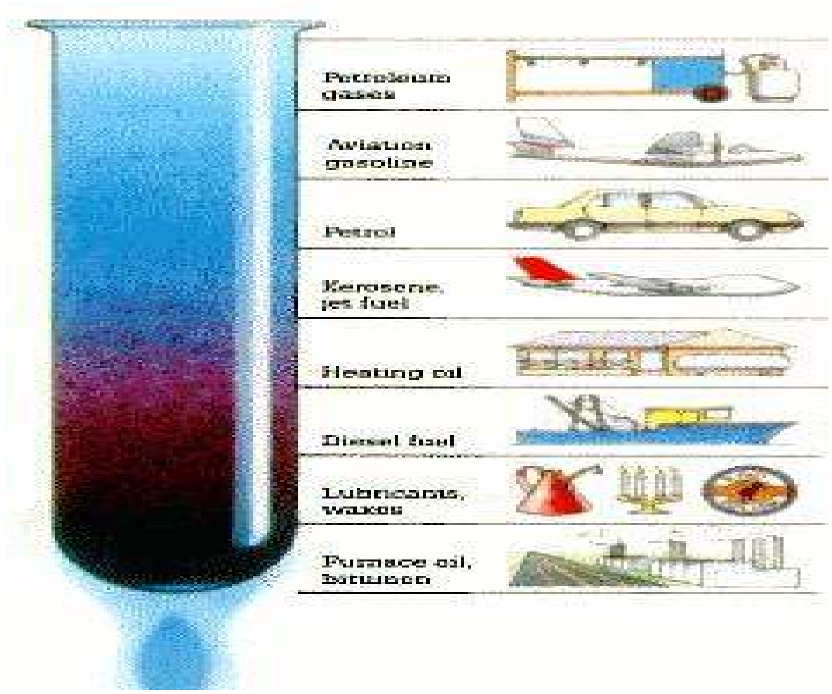


Figure 2.2.Cracking of Crude Oil

2.2.2 Types of Cracking

Cracking processes break down heavier hydrocarbon molecules (high boiling point oils) into lighter products such as petrol and diesel. These processes include catalytic cracking, thermal cracking and hydrocracking.

2.2.2.1 Catalytic Cracking

Catalytic cracking is used to convert heavy hydrocarbon fractions obtained by vacuum distillation into a mixture of more useful products such as petrol and light fuel oil. In this process, the feedstock undergoes a chemical breakdown, under controlled heat (450 - 500^{o}C) and pressure, in the presence of a catalyst - a substance which promotes the reaction without itself being chemically changed. Small pellets of silica - alumina or silica - magnesia have proved to be the most effective catalysts.

The cracking reaction yields petrol, LPG, unsaturated olefin compounds, cracked gas oils, a liquid residue called cycle oil, light gases and a solid coke residue. Cycle oil is recycled to cause further breakdown and the coke, which forms a layer on the catalyst, is removed by burning. The other products are passed through a fractionator to be separated and separately processed.

2.2.2.2 Fluid Catalytic Cracking

Fluid catalytic cracking uses a catalyst in the form of a very fine powder which flows like a liquid when agitated by steam, air or vapour. Feedstock entering the process immediately meets a stream of very hot catalyst and vaporises. The resulting vapours keep the catalyst fluidised as it passes into the reactor, where the cracking takes place and where it is fluidised by the hydrocarbon vapour.

The catalyst next passes to a steam stripping section where most of the volatile hydrocarbons are removed. It then passes to a regenerator vessel where it is fluidised by a mixture of air and the products of combustion which are produced as the coke on the catalyst is burnt off. The catalyst then flows back to the reactor. The catalyst thus undergoes a continuous circulation between the reactor, stripper and regenerator sections.

The catalyst is usually a mixture of aluminium oxide and silica. Most recently, the introduction of synthetic zeolite catalysts has allowed much shorter reaction times and improved yields and octane numbers of the cracked gasolines.

2.2.2.3 Thermal Cracking

Thermal cracking uses heat to break down the residue from vacuum distillation. The lighter elements produced from this process can be made into distillate fuels and petrol. Cracked gases are converted to petrol blending components by alkylation or polymerisation. Naphtha is upgraded to high quality petrol by reforming. Gas oil can be used as diesel fuel or can be converted to petrol by hydrocracking. The heavy residue is converted into residual oil or coke which is used in the manufacture of electrodes, graphite and carbides.

2.2.2.4 Hydrocraking

Hydrocracking can increase the yield of petrol components, as well as being used to produce light distillates. It produces no residues, only light oils. Hydrocracking is catalytic cracking in the presence of hydrogen. The extra hydrogen saturates, or hydrogenates, the chemical bonds of the cracked hydrocarbons and creates isomers with the desired characteristics. Hydrocracking is also a treating process, because the hydrogen combines with contaminants such as sulphur and nitrogen, allowing them to be removed.

Gas oil feed is mixed with hydrogen, heated, and sent to a reactor vessel with a fixed bed catalyst, where cracking and hydrogenation take place. Products are sent to a fractionator to be separated. The hydrogen is recycled. Residue from this reaction is mixed again with hydrogen, reheated, and sent to a second reactor for further cracking under higher temperatures and pressures. In addition to cracked naphtha for making petrol, hydrocracking yields light gases useful for refinery fuel, or alkylation as well as components for high quality fuel oils, lube oils and petrochemical feedstocks.

Following the cracking processes it is necessary to build or rearrange some of the lighter hydrocarbon molecules into high quality petrol or jet fuel blending components or into petrochemicals. The former can be achieved by several chemical process such as alkylation and isomerisation.

2.3 Zeolite as Catalyst

Zeolites occur in nature and have been known for almost 250 years as aluminosilicate minerals. Examples are faujasite, mordenite, offretite, ferrierite, erionite and chabazite. Today, these and other zeolite structures are of great interest in catalysis, yet their naturally occurring forms are of limited value, because (i) they almost always contain undesired impurity phases, (ii) their chemical composition varies from one deposit to another and even from one stratum to another in the same deposit, and (iii) nature did not optimize their properties for catalytic applications.

2.3.1 Structure of Zeolite

The elementary building units of zeolites are SiO_4 and AlO_4 tetrahedra. Adjacent tetrahedra are linked at their corners via the joints among oxygen atoms in each tetrahedron, and these linkages result within an inorganic macromolecule with a structurally distinct three-dimensional framework. The evidence from this building principle that the net formulae of the tetrahedra are SiO_2 and AlO^{-}_2, i.e. one negative charge resides at each tetrahedron in the framework which has an aluminum atom in the center of the entire tetrahedron. The framework of a zeolite contains channels, channel intersections and/or cages with dimensions from 0.2 to 1 nm of the channel's diameter. Inside these voids are water molecules and small cations which compensate the negative framework charge.

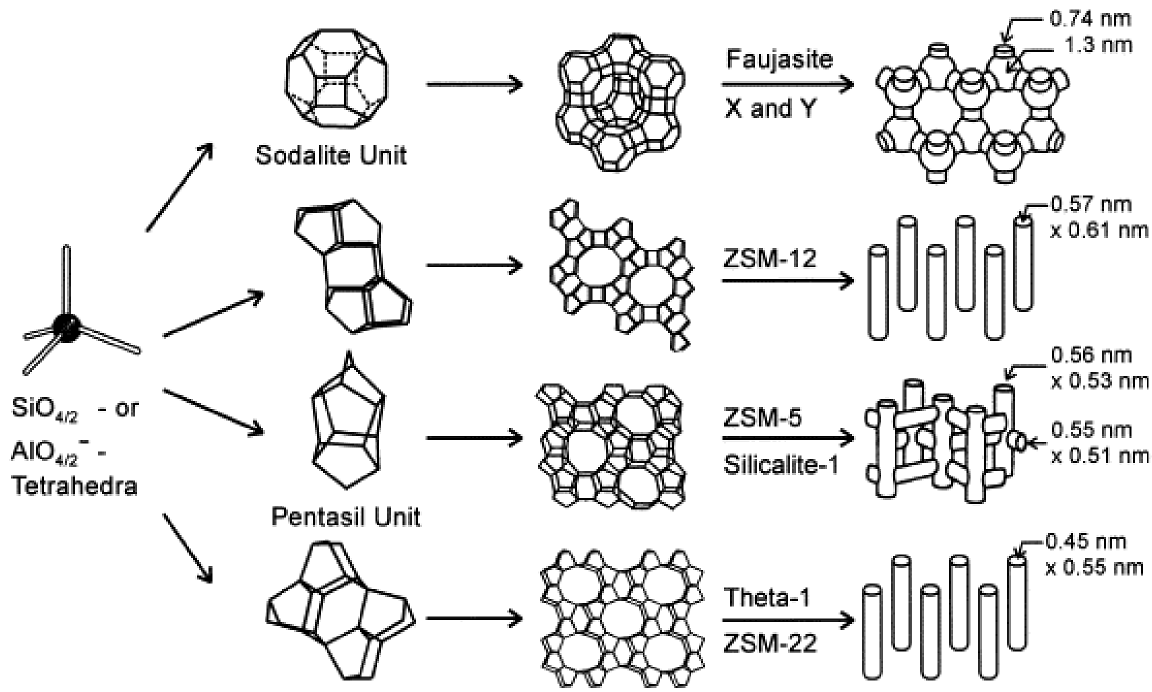
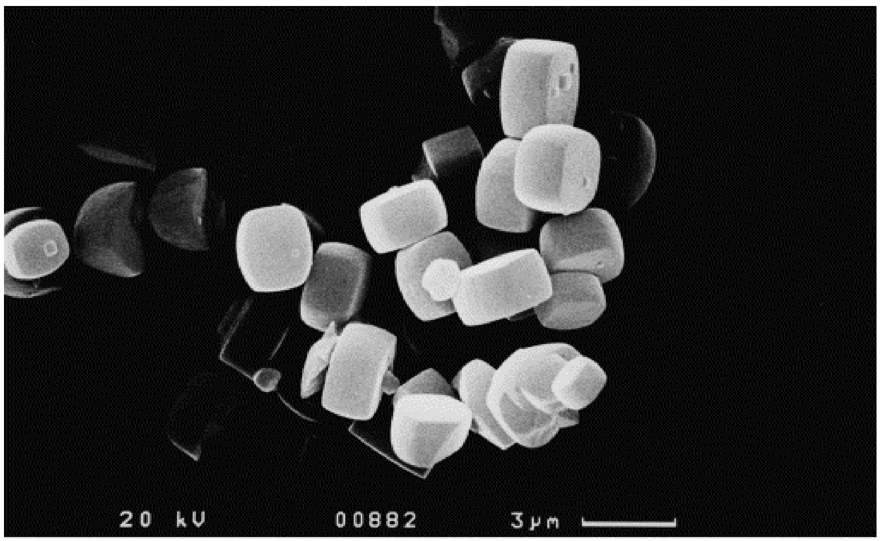


Figure 2.3. Structures of four selected zeolites (from top to bottom: faujasite or zeolites X, Y; zeolite ZSM-12; zeolite ZSM-5 or silicalite-1; zeolite Theta-1 or ZSM-22) and their micropore systems and dimensions.

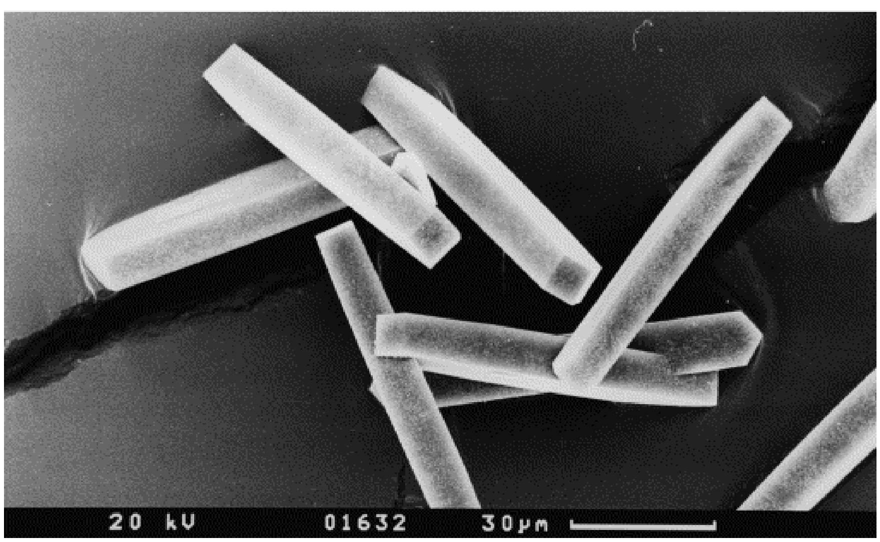
2.3.2 Crystal Size

The size of zeolite crystals is often in the order of one to several micrometers. A typical example is depicted in Fig. 4a which shows tablets of zeolite ZSM-5 with dimensions of 1 to 3 μm. Some zeolites which are relevant to catalysis can, however, be synthesized in very small crystals with a size down to ca. 5 nm (such small crystals are X-ray-amorphous (P.A. Jacobs, E.G. Derouane, J. Weitkamp, J. Chem. Soc. Chem. Comm. (1981) 591) or in very large crystals up to ca. 100 μm or even 1 mm (Springer

Verlag, Berlin, Heidelberg, New York (1998)). As an example, large crystals of zeolite ZSM-5 are shown in Fig. 4b. For catalytic applications, both a decreased and an increased crystal size can be desirable: Upon decreasing the crystal size, the diffusional paths of the reactant and product molecules inside the pores become shorter, and this can result in a reduction or elimination of undesired diffusional limitations of the reaction rate.



(a)



(b)

Figure 2.4 : Scanning electron micrographs showing crystals of zeolite ZSM-5. (a, top): Tablets of ca. 2×2 ×1 μm; (b, bottom): Bars of ca. 80×10×10 μm.

2.4 Chemicals

2.4.1 Isooctane

2,2,4-Trimethylpentane, also known as isooctane, is an octane isomer which defines the 100 point on the octane rating scale. It is an important component of gasoline. Isooctane is targeted as product of biopetrol because petrol itself is dominated by isooctane, with small amount of heptane and a little presence of benzene. Isooctane is derived through isomerization of octane with certain conditions and the presence of catalyst, as performed in petroleum industries. The octane number used as petrol production's parameter to measure the tendency of petrol to auto-ignite and knock in petrol-used engines.

Table 2.1: Physical and chemical properties of isooctane

Synonyms	Isobutyltrimethylpentane, 2,2,4-Trimethylpentane
Appearance	colourless liquid
Molecular formula	C_8H_{18} or $CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$
Molecular weight	114.22 g/mol
Melting point ^0C	-107.38°C
Boiling point ^0C	99.3°C
Density	0.688 g/ml
Specific gravity	0.692
Solubility in water	Immiscible

Since the petrol consists mixture of isooctane and heptane, so the octane number is graded based on composition of both alkanes in petrol. The higher octane number determined represents the higher composition of isooctane in petrol, which gives low tendency to auto-ignite, little knock and smooth burning, which is assigned as petrol with high quality.